A fully *ab initio* potential curve of near-spectroscopic quality for OH⁻ ion: importance of connected quadruple excitations and scalar relativistic effects

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Abstract

A benchmark study has been carried out on the ground-state potential curve of the hydroxyl anion, OH⁻, including detailed calibration of both the 1-particle and n-particle basis sets. The CCSD(T) basis set limit overestimates ω_e by about 10 cm⁻¹, which is only remedied by inclusion of connected quadruple excitations in the coupled cluster expansion — or, equivalently, the inclusion of the 2π orbitals in the active space of a multireference calculation. Upon inclusion of scalar relativistic effects (-3 cm⁻¹ on ω_e), a potential curve of spectroscopic quality (sub-cm⁻¹ accuracy) is obtained. Our best computed EA(OH), 1.828 eV, agrees to three decimal places with the best available experimental value. Our best computed dissociation energies, D_0(OH⁻)=4.7796 eV and D_0(OH)=4.4124 eV, suggest that the experimental D_0(OH)=4.392 eV may possibly be about 0.02 eV too low.

I. INTRODUCTION

Molecular anions play an important role in the chemistry of the interstellar medium [1], of carbon stars [2], and the Earth's ionosphere [3]. As pointed out in Ref. [4], the presence of

anions in the interstellar medium may have profound consequences for our understanding of the interstellar processing of the biogenic elements (see e.g. Ref. [5] and references therein).

Yet as judged from the number of entries in the compilations of Huber and Herzberg [6] (for diatomics) and of Jacox [7] (for polyatomics), high- or even medium-resolution spectroscopic data for anions are relatively scarce compared to the amount of data available for neutral or even cationic species: in the 1992 review of Hirota [8] on spectroscopy of ions, only 13 molecular anions were listed in Table VII, compared to 4 1/2 pages worth of entries for cations. (Early reviews of anion spectroscopy are found in Refs. [9,10], while ab initio studies of structure and spectroscopy of anions were reviewed fairly recently by Botschwina and coworkers [11].) Some of the reasons for this paucity are discussed in the introductions to Refs. [12,4].

One such species is the hydroxyl anion, OH^-. By means of velocity modulation spectroscopy [13], high-resolution fundamentals were obtained [14,15] for three isotopomers, namely $^{16}OH^-$, $^{16}OD^-$, and $^{18}OH^-$; in addition, some pure rotational transitions have been observed [16]. Lineberger and coworkers [17] earlier obtained some rotational data in the course of an electron photodetachment study, and obtained precise electron affinities (EAs) of 14741.03(17) and 14723.92(30) cm^{-1}, respectively, for OH and OD. Very recently, the same group re-measured [18] EA(OH) and obtained essentially the same value but with a higher precision, 14741.02(3) cm^{-1}.

The spectroscopic constants of OH^- were previously the subject of ab initio studies, notably by Werner et al. [19] using multireference configuration interaction (MRCI) methods, and recently by Lee and Dateo (LD) [12] using coupled cluster theory with basis sets as large as $[7s6p5d4f3g2h/6s5p4d3f2g]$.

The LD paper is particularly relevant here. The CCSD(T) (coupled cluster with all single and double substitutions [20] and a quasiperturbative treatment for triple excitations [21]) method, in combination with basis sets of at least $spdfg$ quality and including an account for inner-shell correlation, can routinely predict vibrational band origins of small polyatomic molecules with a mean absolute error on the order of a few cm^{-1} (e.g. for

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C$_2$H$_2$ [22], SO$_2$ [23]). Yet while LD found very good agreement between their computed CCSD(T)/[6s5p4d3f2g/5s4p3d2f] spectroscopic constants and available experimental data, consideration of further basis set expansion and of inner-shell correlation effects leads to a predicted fundamental ν at the CCSD(T) basis set limit of 3566.2±1 cm^{-1}, about 11 cm^{-1} higher than the experimental results [14] of 3555.6057(22) cm^{-1}, where the uncertainty in parentheses represents two standard deviations.

In a recent benchmark study [24] on the ground-state potential curves of the first-row diatomic hydrides using both CCSD(T) and FCI (full configuration interaction) methods, the author found that CCSD(T) has a systematic tendency to overestimate harmonic frequencies of A–H stretching frequencies by on the order of 6 cm^{-1}. Even so, the discrepancy seen by LD is a bit out of the ordinary, and the question arises as to what level of theory is required to obtain 'the right result for the right reason' in this case.

In the present work, we shall show that the discrepancy between the CCSD(T) basis set limit and Nature is mostly due to two factors: (a) neglect of the effect of connected quadruple excitations, and (b) neglect of scalar relativistic effects. When these are properly accounted for, the available vibrational transitions can be reproduced to within a fraction of a cm^{-1} from the computed potential curve. In the context of the present Special Issue, this will also serve as an illustrative example of the type of accuracy that can be achieved for small systems with the present state of the art. Predicted band origins for higher vibrational levels (and 'hot bands') may assist future experimental work on this system. Finally, as by-products of our analysis, we will show that the electron affinity of OH can be reproduced to very high accuracy, and tentatively propose a slight upward revision of the dissociation energy of neutral hydroxyl radical, OH.

II. COMPUTATIONAL METHODS

The coupled cluster, multireference averaged coupled pair functional (ACPF) [25], and full CI calculations were carried out using MOLPRO 98.1 [26] running on DEC/Compaq Alpha workstations in our laboratory, and on the SGI Origin 2000 of the Faculty of Chemistry.

Full CCSDT (coupled cluster theory with all connected single, double and triple excitations [27]) and CCSD(TQ) (CCSD with quasiperturbative corrections for triple and quadruple excitations [28]) calculations were carried out using ACES II [29] on a DEC Alpha workstation.

Correlation consistent basis sets due to Dunning and coworkers [30,31] were used throughout. Since the system under consideration is anionic, the regular cc-pVnZ (correlation consistent polarized valence n-tuple zeta, or VnZ for short) basis sets will be inadequate. We have considered both the aug-cc-pVnZ (augmented correlation consistent, or AVnZ for short) basis sets [32] in which one low-exponent function of each angular momentum is added to both the oxygen and hydrogen basis sets, as well as the aug$'$-cc-pVnZ basis sets [33] in which the addition is not made to the hydrogen basis set. In addition we consider both uncontracted versions of the same basis sets (denoted by the suffix "uc") and the aug-cc-pCVnZ basis sets [34] (ACVnZ) which include added core-valence correlation functions. The largest basis sets considered in this work, aug-cc-pV6Z and aug-cc-pCV5Z, are of [8s7p6d5f4g3h2i/7s6p5d4f3g2h] and [11s10p8d6f4g2h/6s5p4d3f2g] quality, respectively.

The multireference ACPF calculations were carried out from a CASSCF (complete active space SCF) reference wave function with an active space consisting of the valence $(2\sigma)(3\sigma)(1\pi)(4\sigma)$ orbitals as well as the (2π) Rydberg orbitals: this is denoted CAS(8/7)-ACPF (i,e, 8 electrons in 7 orbitals). While the inclusion of the (2π) orbitals is essential (see below), the inclusion of the (5σ) Rydberg orbital (i.e., CAS(8/8)-ACPF) was considered and found to affect computed properties negligibly. In addition, some exploratory CAS-AQCC (averaged quadratic coupled cluster [35]) calculations were also carried out.

Scalar relativistic effects were computed as expectation values of the one-electron Darwin and mass-velocity operators [36,37] for the ACPF wave functions.

The energy was evaluated at 21 points around r_e, with a spacing of 0.01 Å. (All energies were converged to 10^{-12} hartree, or wherever possible to 10^{-13} hartree.) A polynomial in $(r - r_e)/r_e$ of degree 8 or 9 (the latter if an F-test revealed an acceptable statistical significance for the nonic term) was fitted to the energies. Using the procedure detailed in Ref. [24], the Dunham series [38] thus obtained was transformed by derivative matching into

a variable-beta Morse (VBM) potential [39]

$$V_c = D_e \left(1 - \exp[-z(1 + b_1 z + b_2 z^2 + \ldots + b_6 z^6)] \right)^2 \qquad (1)$$

in which $z \equiv \beta(r - r_e)/r_e$, D_e is the (computed or observed) dissociation energy, and β is an adjustable parameter related to that in the Morse function. Analysis of this function was then carried out in two different manners: (a) analytic differentiation with respect to $(r - r_e)/r_e$ up to the 12th derivative followed by a 12th-order Dunham analysis using an adaptation of the ACET program of Ogilvie [40]; and (b) numerical integration of the one-dimensional Schrödinger equation using the algorithm of Balint-Kurti et al. [41], on a grid of 512 points over the interval $0.5a_0$—$5a_0$. As expected, differences between vibrational energies obtained using both methods are negligible up to the seventh vibrational quantum, and still no larger than 0.4 cm^{-1} for the tenth vibrational quantum.

III. RESULTS AND DISCUSSION

A. n-particle calibration

The largest basis set in which we were able to obtain a full CI potential curve was cc-pVDZ+sp(O), which means the standard cc-pVDZ basis set with the diffuse s and p function from aug-cc-pVDZ added to oxygen. A comparison of computed properties for OH$^-$ with different electron correlation methods is given in Table I, while their errors in the total energy relative to full CI are plotted in Figure 1.

It is immediately seen that CCSD(T) exaggerates the curvature of the potential surface, overestimating ω_e by 10 cm^{-1}. In addition, it underestimates the bond length by about 0.0006 Å. These are slightly more pronounced variations on trends previously seen [24] for the OH radical.

The problem does not reside in CCSD(T)'s quasiperturbative treatment of triple excitations: performing a full CCSDT calculation instead lowers ω_e by only 1.7 cm^{-1} and lengthens the bond by less than 0.0001 Å. Quasiperturbative inclusion of connected quadruple excitations, however, using the CCSD(TQ) method, lowers ω_e by 8.5 cm^{-1} relative to CCSD(T),

and slightly lengthens the bond, by 0.00025 Å. (Essentially the same result was obtained by means of the CCSD+TQ* method [42], which differs from CCSD(TQ) in a small sixth-order term E_{6TT}.) No CCSDT(Q) code was available to the author: approximating the CCSDT(Q) energy by the expression $E[CCSDT(Q)] \approx E[CCSDT]+E[CCSD(TQ)]-E[CC5SD(T)] = E[CCSDT] + E_{5QQ} + E_{5QT}$, we obtain a potential curve in fairly good agreement with full CI.

What is the source of the importance of connected quadruple excitations in this case? Analysis of the FCI wave function reveals prominent contributions to the wave function from $(1\pi)^4(2\pi)^0 \rightarrow (1\pi)^2(2\pi)^2$ double excitations; while the (2π) orbitals are LUMO+2 and LUMO+3 rather than LUMO, a large portion of them sits in the same spatial region as the occupied (1π) orbitals. In any proper multireference treatment, the aforementioned excitations would be in the zero-order wave function: obviously, the space of all double excitations therefrom would also entail quadruple excitations with respect to the Hartree-Fock reference, including a connected component.

Since the basis set sizes for which we can hope to perform CCSDT(Q) or similar calculations on this system are quite limited, we considered multireference methods, specifically ACPF from a $[(2\sigma)(3\sigma)(4\sigma)(1\pi)(2\pi)]^8$ reference space (denoted ACPF(8/7) further on). As might be expected, the computed properties are in very close agreement with FCI, except for ω_e being 1.5 cm^{-1} too high. AQCC(8/7) does not appear to represent a further improvement, and adding the (5σ) orbital to the ACPF reference space (i.e. ACPF(8/8)) affects properties only marginally.

B. 1-particle basis set calibration

All relevant results are collected in Table II. Basis set convergence in this system was previously studied in some detail by LD at the CCSD(T) level. Among other things, they noted that ω_e still changes by 4 cm^{-1} upon expanding the basis set from aug-cc-pVQZ to aug-cc-pV5Z. They suggested that ω_e then should be converged to about 1 cm^{-1}; this statement

is corroborated by the CCSD(T)/aug-cc-pV6Z results.

Since the negative charge resides almost exclusively on the oxygen, the temptation exists to use aug′-cc-pVnZ basis sets, i.e. to apply aug-cc-pVnZ only to the oxygen atom but use a regular cc-pVnZ basis set on hydrogen. For n=T, this results in fact in a difference of 10 cm^{-1} on ω_e, but the gap narrows as n increases. Yet extrapolation suggests convergence of the computed fundamental to a value about 1 cm^{-1} higher than the aug-cc-pVnZ curve.

For the AVnZ and A'VnZ basis sets (n=T,Q), the CAS(8/7)-ACPF approach systematically lowers harmonic frequencies by about 8 cm^{-1} compared to CCSD(T); for the fundamental the difference is even slightly larger (9.5 cm^{-1}). Interestingly, this difference decreases for n=5.

It was noted previously [24] that the higher anharmonicity constants exhibit rather greater basis set dependence than one might reasonably have expected, and that this sensitivity is greatly reduced if uncontracted basis sets are employed (which have greater radial flexibility). The same phenomenon is seen here.

In agreement with previous observations by LD, inner-shell correlation reduces the bond lengthen slightly, and increases ω_e by 5–6 cm^{-1}. This occurs both at the CCSD(T) and the CAS(8/7)-ACPF levels.

C. Additional corrections and best estimate

At our highest level of theory so far, namely CAS(8/7)-ACPF(all)/ACV5Z, ν is predicted to be 3559.3 cm^{-1}, still several cm^{-1} higher than experiment. The effects of further basis set improvement can be gauged from the difference between CCSD(T)/AV6Z and CCSD(T)/AV5Z results: one notices an increase of +1.0 cm^{-1} in ω_e and a decrease of 0.00006 Å in r_e. We also performed some calculations with a doubly augmented cc-pV5Z basis set (i.e. d-AV5Z), and found the results to be essentially indistinguishable from those with the singly augmented basis set. Residual imperfections in the electron correlation method can be gauged from the CAS(8/7)-ACPF − FCI difference with our smallest basis set, and appear to consist principally of a contraction of r_e by 0.00004 Å and a decrease in ω_e by 1.5 cm^{-1}.

Adding the two sets of differences to obtain a 'best nonrelativistic' set of spectroscopic constants, we obtain ν=3558.6 cm^{-1}, still 3 cm^{-1} above experiment. In both cases, changes in the anharmonicity constants from the best directly computed results are essentially nil.

Scalar relativistic corrections were computed at the CAS(8/7)-ACPF level with and without the (1s)-like electrons correlated, and with a variety of basis sets. All results are fairly consistent with those obtained at the highest level considered, CAS(8/7)-ACPF(all)/ACVQZ, namely an expansion of r_e by about 0.0001 Å and — most importantly for our purposes — a decrease of ω_e by about 3 cm^{-1}. Effects on the anharmonicity constants are essentially nonexistent.

Upon adding these corrections to our best nonrelativistic spectroscopic constants, we obtain our final best estimates. These lead to ν=3555.44 cm^{-1} for ^{16}OH$^-$, in excellent agreement with the experimental result [14] 3555.6057(22) cm^{-1}. The discrepancy between computed (3544.30 cm^{-1}) and observed [14] (3544.4551(28) cm^{-1}) values for ^{18}OH$^-$ is quite similar. For ^{16}OD$^-$, we obtain ν=2625.31 cm^{-1}, which agrees to better than 0.1 cm^{-1} with the experimental value [15] 2625.332(3) cm^{-1}. Our computed bond length is slightly shorter than the observed one [14] for OH$^-$, but within the error bar of that for OD$^-$ [15]. If we assume an inverse mass dependence for the experimental diabatic bond distance and extrapolate to infinite mass, we obtain an experimentally derived Born-Oppenheimer bond distance of 0.96416(16) cm^{-1}, in perfect agreement with our calculations.

While until recently it was generally assumed that scalar relativistic corrections are not important for first-and second-row systems, it has now been shown repeatedly (e.g. [43–45]) that for kJ/mol accuracy on computed bonding energies, scalar relativistic corrections are indispensable. Very recently, Csaszar et al. [46] considered the effect of scalar relativistic corrections on the ab initio water surface, and found corrections on the same order of magnitude as seen for the hydroxyl anion here. Finally, Bauschlicher [47] compared first-order Darwin and mass-velocity corrections to energetics (for single-reference ACPF wave functions) with more rigorous relativistic methods (specifically, Douglas-Kroll [48]), and found that for first-and second-row systems, the two approaches yield essentially identical results,

lending additional credence to the results of both Csaszar et al. and from the present work. (The same author found [49] more significant deviations for third-row main group systems.)

Is the relativistic effect seen here in OH$^-$ unique to it, or does it occur in the neutral first-row diatomic hydrides as well? Some results obtained for BH, CH, NH, OH, and HF in their respective ground states, and using the same method as for OH$^-$, are collected in Table III. In general, ω_e is slightly lowered, and r_e very slightly stretched — these tendencies becoming more pronounced as one moves from left to right in the Periodic Table. The effect for OH$^-$ appears to be stronger than for the isoelectronic neutral hydride HF, and definitely compared to neutral OH. The excellent agreement (± 1 cm^{-1} on vibrational quanta) previously seen [24] for the first-row diatomic hydrides between experiment and CCSD(T)/ACV5Z potential curves with an FCI correction is at least in part due to a cancellation between the effects of further basis set extension on the one hand, and scalar relativistic effects (neglected in Ref. [24]) on the other hand. The shape of the relativistic contribution to the potential curve is easily understood qualitatively: on average, electrons are somewhat further away from the nucleus in a molecule than in the separated atoms (hence the scalar relativistic contribution to the total energy will be slightly smaller in absolute value at r_e than in the dissociation limit): as one approaches the united atom limit, however, the contribution will obviously increase again. The final result is a slight reduction in both the dissociation energy and on ω_e.

In order to assist future experimental studies on OH$^-$ and its isomers, predicted vibrational quanta $G(n) - G(n-1)$ are given in Table V for various isotopic species, together with some key spectroscopic constants. The VBM parameters of the potential are given in Table IV. The VBM expansion generally converges quite rapidly [39] and, as found previously for OH, parameters b_5 and b_6 are found to be statistically not significant and were omitted.

The VBM expansion requires the insertion of a dissociation energy: we have opted, rather than an experimental value, to use our best calculated value (see next paragraph).

Agreement between computed and observed fundamental frequencies speaks for itself, as does that between computed and observed rotational constants. At first sight agreement

for the rotation-vibration coupling constants α_e is somewhat disappointing. However, for $^{16}OH^-$ and $^{18}OH^-$, the experimentally derived 'α_e' actually corresponds to $B_1 - B_0$, i.e. to $\alpha_e - 2\gamma_e + \ldots$. If we compare the observed $B_1 - B_0$ with the computed $\alpha_e - 2\gamma_e$ instead, excellent agreement is found. In the case of $^{16}OD^-$, the experimentally derived α_e given is actually extrapolated from neutral ^{16}OD: again, agreement between computed and observed $B_1 - B_0$ is rather more satisfying.

We also note that our calculations validate the conclusion by Lee and Dateo that the experimentally derived ω_e and $\omega_e x_e$ for ^{16}OH should be revised upward.

D. Dissociation energies of OH and OH$^-$; electron affinity of OH

This was obtained in the following manner, which is a variant on W2 theory [44]: (a) the CASSCF(8/7) dissociation energy using ACVTZ, ACVQZ, and ACV5Z basis sets was extrapolated geometrically using the geometric formula $A + B/C^n$ first proposed by Feller [50]; (b) the dynamical correlation component (defined at CAS(8/7)-ACPF(all) $-$ CASSCF(8/7)) of the dissociation energy was extrapolated to infinite maximum angular momentum in the basis set, $l \to \infty$ from the ACVQZ (l=4) and ACV5Z (l=5) results using the formula [51] $A + B/l^3$; (c) the scalar relativistic contribution obtained at the CAS(8/7)-ACPF level was added to the total, as was the spin-orbit splitting [52] for O$^-$(^2P). Our final result, D_0=4.7796 eV, is about 0.02 eV higher than the experimental one [6]; interestingly enough, the same is true for the OH radical (computed D_0=4.4124 eV, observed 4.392 eV). In combination with either the experimental electron affinity of oxygen atom, EA(O)=1.461122(3) eV [53] or the best computed EA(O)=1.46075 eV [54], this leads to electron affinities of OH, EA(OH)=1.8283 eV and 1.8280 eV, respectively, which agree to three decimal places with the experimental value [18] 1.827611(4) eV. We note that the experimental D_e(OH$^-$) is derived from D_e(OH)+EA(OH)$-$EA(O), and that a previous calibration study on the atomization energies of the first-row hydrides [55] suggested that the experimental D_e(OH) may be too low. While a systematic error in the electronic structure treatment that cancels almost exactly between OH and OH$^-$ cannot entirely be ruled out, the excellent agreement

obtained for the electron affinity does lend support to the computed D_e values.

IV. CONCLUSIONS

We have been able to obtain a fully ab initio radial function of spectroscopic quality for the hydroxyl anion. In order to obtain accurate results for this system, inclusion of connected quadruple excitations (in a coupled cluster expansion) is imperative, as is an account for scalar relativistic effects. Basis set expansion effects beyond $spdfgh$ take a distant third place in importance. While consideration of connected quadruple excitation effects and of basis set expansion effects beyond $spdfgh$ would at present be prohibitively expensive for studies of larger anions, no such impediment would appear to exist for inclusion of the scalar relativistic effects (at least for one-electron Darwin and mass-velocity terms).

Our best computed EA(OH), 1.828 eV, agrees to three decimal places with the best available experimental value. Our best computed dissociation energies, $D_0(\mathrm{OH}^-)$=4.7796 eV and $D_0(\mathrm{OH})$=4.4124 eV, suggest that the experimental $D_0(\mathrm{OH})$=4.392 eV (from which the experimental $D_0(\mathrm{OH}^-)$ was derived by a thermodynamic cycle) may possibly be about 0.02 eV too low.

One of the purposes of the paper by Lee and Dateo [12] was to point out to the scientific community, and in particular the experimental community, that state-of-the art ab initio methods now have the capability to predict the spectroscopic constants of molecular anions with sufficient reliability to permit assignment of a congested spectrum from an uncontrolled environment — such as an astronomical observation — on the basis of the theoretical calculations alone. The present work would appear to support this assertion beyond any doubt.

REFERENCES

[1] W. W. Duley and T. J. Millar, Astrophys. J. 220(1978)124; H.-H. Lee, R. P. A. Bettens, and E. Herbst, Astron. Astrophys., Suppl. Ser. 119(1996)111

[2] M. S. Vardya and K. S. Krishnaswamy, Chem. Phys. Lett. 73(1980)616; G. Wallerstein, Astron. Astrophys. 105(1982)219 B. D. Rehfuss, D.-J. Liu, B. M. Dinelli, M.-F. Jagod, W. C. Ho, M. W. Crofton, and T. Oka, J. Chem. Phys. 89(1988)129

[3] R. P. Wayne, Chemistry of Atmospheres, 2nd ed. (Clarendon Press, Oxford, 1991).

[4] T. J. Lee and C. E. Dateo, Spectrochimica Acta A 55(1999)739

[5] L. Allamandola, M. P. Bernstein, and S. A. Sanford, in C. B. Cosmovici, S. Bowyer, D. Wertheimer (Eds.), *Astronomical and Biochemical Origins and the Search for Life in the Universe*, Editrice Compositori, Bologna, 1997, pp. 23–47.

[6] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979)

[7] M. E. Jacox, *J. Phys. Chem. Ref. Data* Monograph **3** (1994); M. E. Jacox, J. Phys. Chem. Ref. Data 27(1998)115; http://webbook.nist.gov/chemistry/polyatom/

[8] E. Hirota, Chem. Rev. 92(1992)141

[9] T. Amano, Phil. Trans. Royal Soc. (London) A 324(1988)163

[10] J. Owrutsky, N. Rosenbaum, L. Tack, M. Gruebele, M. Polak, and R. J. Saykally, Phil. Trans. Royal Soc. (London) A 324(1988)97; R. J. Saykally, Science 239(1988)157

[11] P. Botschwina, S. Seeger, M. Mladenović, B. Schulz, M. Horn, S. Schmatz, J. Flügge, and R. Oswald, Int. Rev. Phys. Chem. 14(1995)169

[12] T. J. Lee and C. E. Dateo, J. Chem. Phys. 107(1997)10373

[13] C. S. Gudeman and R. J. Saykally, Ann. Rev. Phys. Chem. 35(1984)387

[14] N. H. Rosenbaum, J. C. Owrutsky, L. M. Tack, and R. J. Saykally, J. Chem. Phys. 84(1986)5308; see also preliminary communication, J. C. Owrutsky, N. H. Rosenbaum, L. M. Tack, and R. J. Saykally, J. Chem. Phys. 83(1985)5338.

[15] B. D. Rehfuss, M. W. Crofton, and T. Oka, J. Chem. Phys. 85(1986)1785

[16] D. J. Liu and T. Oka, J. Chem. Phys. 84(1986)2426

[17] P. A. Schulz, R. D. Mead, P. L. Jones, and W. C. Lineberger, J. Chem. Phys. 77(1982)1153

[18] J. R. Smith, J. B. Kim, and W. C. Lineberger, Phys. Rev. A 55(1997)2036

[19] H.-J. Werner, P. Rosmus, and E.-A. Reinsch, J. Chem. Phys. 79(1983)905

[20] G. D. Purvis III and R. J. Bartlett, J. Chem. Phys. 76(1982)1910

[21] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. 157(1989)479

[22] J. M. L. Martin, T. J. Lee, and P. R. Taylor, J. Chem. Phys. 108(1998)676.

[23] J. M. L. Martin, J. Chem. Phys. 108(1998)2791

[24] J. M. L. Martin, Chem. Phys. Lett. 292(1998)411

[25] R. J. Gdanitz and R. Ahlrichs, Chem. Phys. Lett. 143(1988)413

[26] MOLPRO is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, A. W. Lloyd, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schütz, H. Stoll, and T. Thorsteinsson. `http://www.tc.bham.ac.uk/molpro/`

[27] J. Noga and R. J. Bartlett, J. Chem. Phys. 86(1987)7041 erratum 89(1988)3401

[28] S. A. Kucharski and R. J. Bartlett, Chem. Phys. Lett. 158(1989)550; K. Raghavachari,

J. A. Pople, E. S. Replogle, and M. Head-Gordon, J. Phys. Chem. 94(1990)5579

[29] J. F. Stanton, J. Gauss, J. D. Watts, W. Lauderdale, and R. J. Bartlett, (1996) ACES II, an ab initio program system, incorporating the MOLECULE vectorized molecular integral program by J. Almlöf and P. R. Taylor, and a modified version of the ABACUS integral derivative package by T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, and P. R. Taylor.

[30] T. H. Dunning Jr., J. Chem. Phys. 90(1989)1007.

[31] T.H. Dunning, Jr., K.A. Peterson, and D.E. Woon, "Correlation consistent basis sets for molecular calculations", in *Encyclopedia of Computational Chemistry*, ed. P. von Ragué Schleyer, (Wiley & Sons, Chichester, 1998).

[32] R. A. Kendall, T. H. Dunning, and R. J. Harrison, J. Chem. Phys. 96(1992)6796

[33] J. E. Del Bene, J. Phys. Chem. 97(1993)107

[34] D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. 103(1995)4572

[35] P. G. Szalay and R. J. Bartlett, Chem. Phys. Lett. 214(1993)481

[36] R. D. Cowan and M. Griffin, J. Opt. Soc. Am. 66(1976)1010

[37] R. L. Martin, J. Phys. Chem. 87(1983)750

[38] J. L. Dunham, Phys. Rev. 41(1932)721

[39] J. A. Coxon, J. Mol. Spectrosc. 152(1992)274 and references therein. The VBM function with the exponent truncated at the b_2 term was originally proposed (under the name 'generalized Morse function') by P. J. Kuntz and A. C. Roach, J. Chem. Soc. Faraday Trans. II 68(1972)259

[40] J. F. Ogilvie, Comput. Phys. Commun. 30(1983)101; CPC library program ACET

[41] G.G. Balint-Kurti, C.L. Ward, and C.C. Marston, Comput. Phys. Commun. 67(1991)285; CPC library program ABCQ.

[42] R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, Chem. Phys. Lett. 165(1990)513

[43] C. W. Bauschlicher Jr. and A. Ricca, J. Phys. Chem. A 102(1998)8044

[44] J. M. L. Martin and G. De Oliveira, J. Chem. Phys. 111(1999)1843

[45] C. W. Bauschlicher Jr., J. M. L. Martin, and P. R. Taylor, J. Phys. Chem. A 103(1999)7715

[46] A. G. Csaszar, J. S. Kain, O. L. Polyansky, N. F. Zobov, and J. Tennyson, Chem. Phys. Lett. 293(1998)317; erratum 312(1999)613

[47] C. W. Bauschlicher Jr., J. Phys. Chem. A 104(2000)2281

[48] M. Douglas and N. M. Kroll, Ann. Phys. (NY) 82(1974)89; R. Samzow, B. A. Heß, and G. Jansen, J. Chem. Phys. 96(1992)1227 and references therein.

[49] C. W. Bauschlicher Jr., Theor. Chem. Acc. 101(1999)421

[50] D. Feller, J. Chem. Phys. 96(1992)6104

[51] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, Chem. Phys. Lett. 286(1998)243

[52] C. E. Moore, *Atomic energy levels*, Natl. Bur. Stand. (US) Circ. **1949**, *467*.

[53] D. M. Neumark, K. R. Lykke, T. Andersen, and W. C. Lineberger, Phys. Rev. A 32(1985)1890 a recent review proposes a minor revision to 1.4611107(17) eV: C. Blondel, Phys. Scr. T58(1995)31

[54] G. De Oliveira, J. M. L. Martin, F. De Proft, and P. Geerlings, Phys. Rev. A 60(1999)1034

[55] J. M. L. Martin, Chem. Phys. Lett. 273(1997)98

TABLES

TABLE I. Computed total energy (hartree), bond distance (Å), harmonic frequency (cm^{-1}) and anharmonicity constants (cm^{-1}) of $^{16}OH^-$ using the cc-pVDZ+sp(O) basis set as a function of the electron correlation method

	E_e	r_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	$\omega_e z_e$
FCI	-75.623457	0.97503	3701.7	96.65	0.454	-0.024
CCSD	-75.616478	0.97209	3747.1	95.28	0.537	-0.010
CCSD(T)	-75.622380	0.97442	3711.6	96.45	0.401	-0.031
CC5SD(T)	-75.621379	0.97428	3709.5	97.74	0.367	-0.025
CCSDT	-75.622656	0.97449	3709.9	96.37	0.465	-0.023
CCSD(TQ)	-75.621660	0.97467	3703.1	98.17	0.352	-0.024
CCSD+TQ*	-75.621473	0.97463	3702.8	98.48	0.337	-0.023
approx. CCSDT(Q)	-75.622937	0.97488	3703.5	96.78	0.452	-0.022
approx. CCSDT+Q*	-75.622750	0.97484	3703.2	97.10	0.438	-0.020
CAS(8/7)-ACPF	-75.623089	0.97499	3703.2	96.60	0.455	-0.023
CAS(8/7)-AQCC	-75.622147	0.97500	3702.9	96.54	0.456	-0.029
CAS(8/8)-ACPF	-75.623084	0.97501	3703.0	96.66	0.444	-0.024
CAS(8/8)-AQCC	-75.622669	0.97493	3704.2	96.59	0.443	-0.024

TABLE II. Computed bond distance, harmonic frequency, anharmonicity constants, and Dunham correction to harmonic frequency for $^{16}OH^-$ as a function of basis set and electron correlation method. All data in cm^{-1} except r_e (Å)

Corr. method	basis set	1s corr?	r_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	$\omega_e z_e$	$Y_{10} - \omega_e$	ν
CAS(8/7)-ACPF	aug'-cc-pVTZ	no	0.96776	3725.01	92.738	0.3623	-0.0566	-0.37	3540.07
CAS(8/7)-ACPF	aug'-cc-pVQZ	no	0.96517	3742.24	93.610	0.3855	-0.0068	-0.24	3556.00
CAS(8/7)-ACPF	aug'-cc-pVQZ	no+REL	0.96528	3739.00	93.564	0.3881	-0.0066	-0.24	3552.86
CAS(8/7)-ACPF	aug'-cc-pV5Z	no	0.96476	3745.58	93.856	0.4968	-0.0192	-0.14	3559.24
CCSD(T)	aug'-cc-pVTZ	no	0.96741	3733.55	91.987	0.3284	-0.0524	-0.40	3549.99
CCSD(T)	aug'-cc-pVQZ	no	0.96486	3750.37	92.948	0.3474	-0.0121	-0.27	3565.28
CCSD(T)	aug'-cc-pV5Z	no	0.96456	3751.56	93.183	0.4643	-0.0227	-0.17	3566.42
CAS(8/7)-ACPF	AVTZ	no	0.96809	3716.44	92.083	0.2144	-0.0133	-0.42	3532.49
CAS(8/7)-ACPF	AVQZ	no	0.96551	3737.30	93.868	0.4277	-0.0034	-0.19	3550.75
CAS(8/7)-ACPF	AV5Z	no	0.96488	3744.47	93.816	0.5236	-0.0157	-0.13	3558.33
CCSD(T)	AVTZ	no	0.96781	3723.56	91.345	0.1745	-0.0188	-0.46	3540.88
CCSD(T)	AVQZ	no	0.96520	3745.61	93.159	0.3900	-0.0107	-0.22	3560.29
CCSD(T)	AV5Z	no	0.96472	3749.39	93.193	0.4966	-0.0291	-0.15	3564.32
CCSD(T)	d-AV5Z	no	0.96476	3749.31	93.079	0.4900	-0.0283	-0.16	3564.45
CCSD(T)	AV6Z	no	0.96466	3750.41	93.237	0.4839	-0.0214	-0.14	3565.26
CCSD(T)	AVTZuc	no	0.96734	3724.84	92.600	0.4875	-0.0734	-0.39	3540.46
CCSD(T)	AVQZuc	no	0.96522	3744.72	93.044	0.4081	-0.0219	-0.27	3559.58
CCSD(T)	AV5Zuc	no	0.96473	3749.21	93.243	0.4435	-0.0103	-0.16	3563.95
CAS(8/7)-ACPF	ACVTZ	no	0.96789	3713.45	91.642	0.2137	0.0000	-0.41	3530.45
CAS(8/7)-ACPF	ACVQZ	no	0.96558	3735.72	93.894	0.4219	-0.0130	-0.23	3549.01
CAS(8/7)-ACPF	ACV5Z	no	0.96501	3740.66	94.081	0.4691	-0.0005	-0.14	3553.87
CCSD(T)	ACVTZ	no	0.96768	3718.89	91.145	0.1639	-0.0044	-0.45	3536.66
CCSD(T)	ACVQZ	no	0.96525	3744.90	93.038	0.3867	-0.0191	-0.26	3559.73
CCSD(T)	ACV5Z	no	0.96472	3749.22	93.225	0.4361	-0.0101	-0.17	3563.96
CAS(8/7)-ACPF	ACVTZ	yes	0.96725	3714.74	92.017	0.1855	-0.0035	-0.43	3530.86
CAS(8/7)-ACPF	ACVQZ	yes	0.96468	3741.86	94.110	0.4205	-0.0129	-0.23	3554.71
CAS(8/7)-ACPF	ACV5Z	yes	0.96410	3746.51	94.317	0.4682	0.0009	-0.14	3559.26
CCSD(T)	ACVTZ	yes	0.96688	3725.04	91.122	0.1509	-0.0022	-0.46	3542.81
CCSD(T)	ACVQZ	yes	0.96435	3751.76	93.151	0.3929	-0.0202	-0.26	3566.37
CCSD(T)	ACV5Z	yes	0.96378	3756.27	93.347	0.4427	-0.0088	-0.17	3570.80
CAS(8/7)-ACPF	ACVQZ all	yes+REL	0.96478	3738.69	94.098	0.4193	-0.0102	-0.24	3551.57
ΔREL			0.00010	-3.17	-0.012	-0.0012	0.0027	-0.01	-3.14
best calc.			0.96417	3742.87	94.404	0.4527	0.0100	-0.14	3555.44

The suffix "+REL" indicates inclusion of scalar relativistic (Darwin and mass-velocity) effects obtained as expectation values for the wave function indicated.

TABLE III. Effect of scalar relativistic contributions on the bond lengths (Å) and harmonic frequencies (cm^{-1}) of the AH (A=B–F) diatomics. All calculations were carried out at the CAS($2\sigma3\sigma4\sigma1\pi$)-ACPF/ACVQZ level with all electrons correlated

	Δr_e	$\Delta\omega_e$
BH	-0.00001	-0.57
CH	+0.00001	-1.08
NH	+0.00003	-1.77
OH	+0.00004	-2.35
HF	+0.00005	-2.80
OH$^-$	+0.00010	-3.14

Effects on the anharmonicity constants are negligible.

TABLE IV. Parameters for the VBM representation, eq. (1), obtained from our best potential. D_e, r_e are in cm^{-1} and Å, respectively; the remaining parameters are dimensionless

D_e	40398.7079
r_e	0.964172
β	2.128977
b_1	-0.047181
b_2	0.022371
b_3	-0.0070906
b_4	0.0018429

TABLE V. Spectroscopic constants and band origins (in cm^{-1}) of different isotopomers of the hydroxyl anion obtained from our best potential

	^{16}OH$^-$		^{16}OD$^-$		^{18}OH$^-$		^{18}OD$^-$
	calc	obsd[a]	calc	obsd[b]	calc	obsd[a]	calc
Y_{00}	2.38		1.26		2.36		1.25
$Y_{10} \approx \omega_e$	3742.72	3738.44(99)[c]	2724.79	2723.5(10)	3730.35		2707.77
$-Y_{20} \approx \omega_e x e$	94.298	91.42(49)[c]	49.979	49.72(50)	93.676		49.357
$Y_{30} \approx \omega_e y e$	0.4686		0.1808	0.38(15)	0.4639		0.1774
$Y_{01} \approx B_e$	19.126021	19.12087(37)	10.136936	10.13599(30)	18.999788	18.99518(49)	10.010698
$-Y_{11} \approx \alpha_e$	0.779874	0.77167(13)	0.300914	0.3043(5)	0.772165	0.76409(16)	0.295310
$Y_{21} \approx \gamma_e$	0.003913		0.001099		0.003861		0.001072
α_e-2γ_e	0.772048	0.77167(13)	0.298716	0.2984(3)	0.764443	0.76409(16)	0.293166
$-Y_{02} \approx D_e$	0.001998	0.001995(6)	0.000561	0.000559(2)[d]	0.001972	0.000031(2)	0.000547
$Y_{12} \approx \beta_e$	0.000032	0.000032(2)	0.000006	0.000008(2)	0.000031	0.000031(2)	0.000006
ZPVE	1850.23		1351.19		1844.18		1342.81
G(1)-G(0)	3555.63	3555.6057(22)	2625.42	2625.332(3)	3544.49	3444.4551(28)	2609.63
G(2)-G(1)	3371.17		2527.06		3361.24		2512.49
G(3)-G(2)	3189.42		2429.75		3180.66		2416.38
G(4)-G(3)	3010.39		2333.49		3002.78		2321.29
G(5)-G(4)	2834.11		2238.28		2827.63		2227.23
G(6)-G(5)	2660.70		2144.12		2655.31		2134.21
G(7)-G(6)	2490.31		2051.03		2485.97		2042.24

The Dunham constants Y_{mn} include higher-order corrections to the mechanical spectroscopic constants (like $\omega_e, \omega_e x_e$) as obtained from the potential function.

(a) Ref. [14]. Uncertainties in parentheses correspond to two standard deviations.

(b) Ref. [15]. Uncertainties in parentheses correspond to three standard deviations.

(c) LD proposed ω_e=3741.0(14) and $\omega_e x_e$=93.81(93) cm^{-1}, obtained by mass scaling of the ^{16}OD$^-$ results, as more reliable.

(d) From observed D_0 and D_1 in Ref. [15].

FIG. 1. Deviation from the FCI potential curve of OH$^-$ for different electron correlation methods